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FLUORESCENCE EXCITATION STUDIES OF MOLECULAR PHOTOIONIZATION IN EXTERNAL ELECTRIC FIELDS*

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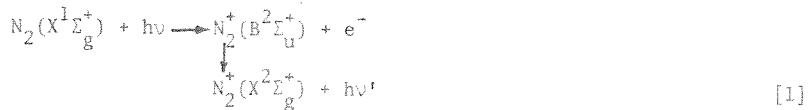
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ABSTRACT

With molecular nitrogen used as an example, it is shown that partial photoionization cross-sections for gas samples in external electric fields can be obtained through fluorescence excitation spectroscopy.

Studies of photoionization dynamics in external electric fields have enhanced our understanding of photoionization generally and have stimulated a great deal of theoretical progress.¹⁻⁴ The work reported here demonstrates that in an electric field, fluorescence excitation spectroscopy provides relative partial photoionization cross-sections for the excited ionic state.⁵ These measurements extend present experimental capabilities that probe photoionization in external fields, because existing methods (e.g., photoabsorption spectroscopy and photoionization mass spectrometry) are limited to the study of total photoionization cross-sections. Molecular nitrogen was investigated in the present work, with the excitation/fluorescence sequence given below:



The fluorescence intensity from the B state of N_2^+ was monitored as a function of the excitation wavelength. The partial photoionization cross-section for the $\text{N}_2^+(\text{B}^2\Sigma_u^+)$ state is very small compared with the total photoionization cross-section,^{6,7} underscoring the point that even extremely weak channels in atomic or molecular photoionization may be studied selectively.

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The experiment is performed by intersecting monochromatized VUV radiation (0.3 \AA bandwidth) from SURF-II (Synchrotron Ultraviolet Radiation Facility at the U. S. National Bureau of Standards) with a gas sample exiting from an effusive jet. The electric field is produced using two parallel grids. The fluorescence radiation is collected by a planoconvex lens and detected by a cooled photomultiplier tube. At each excitation wavelength, correction is made for the detector dark counts by closing a shutter in front of the photomultiplier.

The results are plotted in Fig. 1. The intensity of normalized, undispersed N_2^+ B-X fluorescence vs. excitation wavelength is shown for different values of the field strength. The B-state threshold systematically shifts to lower energy as the field is increased.

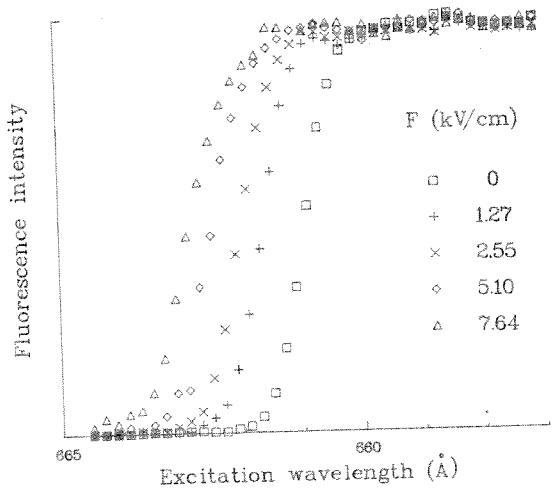


Figure 1
Normalized fluorescence excitation spectra of nitrogen (sequence of eqn. [1]), for selected values of the electric field strength.

We stress that this threshold is unobservable in photoabsorption or photoionization spectra. Moreover, because the threshold shown here is not obscured by intense autoionization features, the behavior under the influence of the field may be analyzed precisely. The energy shift of the threshold is plotted as a function of the square root of the electric field strength, $(F)^{\frac{1}{2}}$, in Fig. 2, and a linear relationship results. Also plotted in Fig. 2 (dashed line) is the linear dependence predicted classically for photoionization of atomic hydrogen.⁴ The slope for N_2 differs from that expected for the H atom, reflecting the non-zero quantum defects of the photoelectron exit channels which populate the B state of the nitrogen ion. The data are being analyzed within this framework.

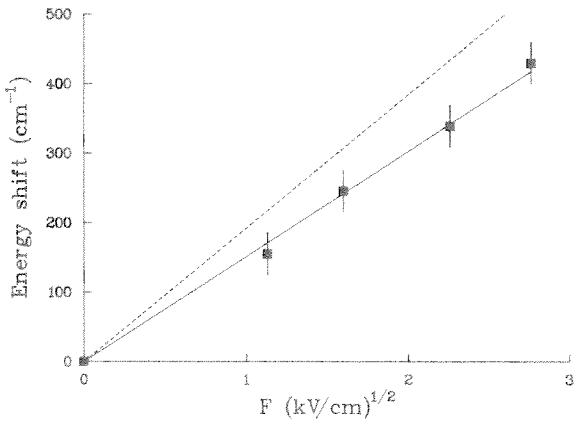


Figure 2

Ionization threshold energy shift vs. square root of applied electric field for molecular nitrogen (data points, solid line), and atomic hydrogen (predicted,⁴ dashed line).

These results illustrate the key point - fluorescence excitation spectroscopy may be utilized under electric field conditions so that thresholds other than the ground ionic state may be selectively probed. For the N₂ case presented, this permitted the observation of very clear threshold behavior. Such measurements also allow other types of studies, including determinations of partial photoionization cross-sections for systems with strong autoionization pathways. We have initiated an investigation of CO₂⁺ A²Π_u → X²Π_g fluorescence for which the excitation spectrum shows strong superimposed resonance contributions from autoionization.⁸ The A-state threshold shifts to lower energy with increasing applied field, and the fluorescence spectra also reveal autoionizing Rydberg states which lie below the zero-field threshold. The technique described here should be of general utility for studies of atomic and molecular photoionization in an electric field. It extends current capabilities by providing detailed measurements of photoionization thresholds for excited electronic states of ions.

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